**Patent Application**

**Method for separating polymer systems and pore-free polymer films used in said method**

5   Polymers and the products manufactured thereof have a very significant industrial importance. This is due to, among others, characteristics such as e.g. long product life, insensitivity against many chemicals, elasticity or hardness, transparency, electric resistance, special optical

10  characteristics and, often, their low thermal conductivity. Polymers, in the sense of the present invention, are synthetic polycondensates, addition polymers or polymerizates, but also natural long-chain compounds. The chain architecture (linear, branched, block-like structure of

15  different elements) and the stereo chemistry (atactic, syndiotactic, isotactic) of the yielding polymer as well as the molecular weight (chain length) can indeed be controlled by appropriate selection of the process parameters; however, as with all syntheses in organic chemistry, the formation of

20  byproducts, the formation of chains of various lengths as well as chains with objectionable stereo chemistry are unavoidable. In many cases, this has negative effects on the characteristics and applications. A separation of the reaction mixture is therefore, in many cases, necessary.

25

There are numerous methods for the separation of macromolecules from their mixture of low-/high-molecular substances in the current technical state of the art. These include selective precipitation from a solution, fractionated

30  crystallization, likewise from solution, as well as gel chromatographic methods. Within a range of methods, the separation effect is based on a size exclusion (J. Porath, P.

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Flodin, Nature 183, 1657 (1959); J.C.Moore, J. Polym. Sci,
A2, 835 (1954); W.W.Yau, J.J.Kirkland, D.D.Bly, Modern Size
Exclusion Liquid Chromatography: Practice of Gel Permeation
and Gel Filtration Chromatography, Wiley, N.Y. (1979);

5 J.V.Dankins, in Comprehensive Polymer Science, Vol. I, p.
231, G.Allen, J. Bevington eds, Pergamon Press, Oxford
(1989)).

During gel filtration chromatography (GFC) or gel permeation
10 chromatography (GPC), a solution containing the polymers is
sent through a column filled with gel particles containing
various sized pores. The separation takes place through the
accessibility of the gels' pores as a function of the
particle size and, therefore, also the molecular weight. The
15 decisive value is the hydrodynamic volume $V_h$. If the latter
is equal for different polymers or particles respectively
(e.g. polystyrene and polymethylmethacrylate or also coils
and/or compact spheres), no separation takes place. The
aforementioned methods serve especially to characterize
20 according to size or hydrodynamic volume. A separation of
substances is limited to very small quantities which are
typically measured in a scale smaller than grams.  The
separation by means of gel-chromatography is strongly limited
concerning the throughput quantity. DE 3831970 A1 and DE
25 3934068 A1 describe particles to be used within the gel
permeation chromatography. These particles allow for the
separation of polymeric substances according to their size or
their hydrodynamic volume, whereby the throughput is limited
to the scale of grams.

30

A further type of separation method is characterized by
exposure to a field which might be electrical, thermal or an
electromagnetic flux, in a perpendicular direction to the
solvent flow containing the substances to be separated (J.C.

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Giddings, K.A. Graff, K.D. Caldwell, M.N. Myers in Advances in Chromatography, p. 203; C.D. Craver ed., Dekker N.Y. 1983; J.J. Gunderson, J.C. Giddings, in Comprehensive Polymer Science, Vol. I, p. 279, G. Allen, J. Bevington eds, Pergamon

5    Press, Oxford (1989)). These fields cause a spatial separation of different substances according to the coupling to the field, resulting in allocation to different layers of laminar flows. Compared with GFC and GPC, these methods have the advantage that they not only discriminate in regard to

10   the hydrodynamic volume, but also, e.g., according to electrical parameters caused by a specific chemical structure. Among the disadvantages of this method are its limitation to low concentrations in order to avoid overloading, the limitation regarding the effectively

15   separable quantity as well as the fact that wide distributions at the respective heading and tailing are not dissolved. The quantity limitation does not apply as strictly to a fractionation of varying solubilities in predetermined solvents (R. Koningsveld, L.A.Kleinjens, H.Geerissen,

20   P.Schützeichel, B.A.Wolf, Comprehensive Polymer Science, Vol. I, p. 293; G.Allen, J. Bevington eds, Pergamon Press, Oxford (1989); B.A.Wolf, Adv. Polym. Sci. 10, 109 (1972)). Further methods, such as thin layer chromatography (TLC), play a marginal role in a characterization of the molecular

25   weight distribution and play no role at all concerning a quantitative separation (H. Inagaki, Adv. Polym. Sci 24, 189 (1977)).

To date, with the help of gel-chromatographic and

30   electrophoretic methods, biopolymers such as DNA and RNA fragments with masses up to 20-40 kB (agarose gel) or 1000 kB (pulse gel electrophoresis) respectively, can be separated (J. Sambrook, E.F. Fritsch, T. Maniatis: Molecular cloning: A Laboratory Manual, 2nd Edition (1989)).

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Separations of biopolymers, as for example nucleic acids, with the help of spherical magnetic silica particles with adjustable particle size and adjustable magnetic content are

5   described in DE 10035953 A1. DE 69026090 T2 describes the fractionation in counter migration with the help of capillary electrophoresis, and DE 69221969 T2 describes polymer solutions for capillary electrophoresis, with the help of which biological molecules with molecule masses up to a few

10  kDa can be separated. Both methods serve to separate proteins and nucleic acids. The separation of proteins with magnetic silica gel particles is limited to the milligram scale, the capillary electrophoresis to the picogram scale.

15  DE 3851616 T2 describes macroporous polymer membranes with thicknesses in the millimeter scale which possess a globular (spherical) microstructure with communing free spaces in between. In this method, the membranes serve as adsorbents for the components of the mixture to be separated.

20  Subsequently, these components are successively eluted, with the help of suitable eluents. With the help of these polymer membranes, synthetic polymers and biopolymers can be separated in the gram scale.

25  However, until now, it has proved very difficult to separate mixtures of macromolecular and, in particular, polymer systems in quantities above the gram scale. Thus, DE 4214527 C2 describes a method for the processing of packaging materials which contain one or more polymers, by dissolving

30  the polymer portions in organic solvents and subsequently thermally processing them into products with monomer character. This method allows for the application of polymer mixtures in the kilogram scale and delivers pure grade

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separated products; however, the polymer character is lost during the purification process.

While separating non-polymer substance mixtures and the
5  purification of substances in the gaseous phase and in the liquid phase, with the help of polymers and polymer systems, one frequently utilizes the adsorption and permeation characteristics of polymers. On the one hand, many polymers are able to adsorb substances which afterwards can be
10  selectively re-dissolved; on the other hand, many polymers are permeable for other, gaseous substances. Thus, they can be penetrated by them.

DE 69505583 T2 describes polymer membranes, with the help of
15  which organic solvents can be separated from aqueous solvents. A greater throughput quantity of the mixture to be separated is thereby possible; however, only organic molecules with molecule masses of up to approx. 200 g/mol can be separated. Similar facts apply for the separation of
20  acidic gasses from gaseous mixtures which is described in DE 19600954 C2, and for the membrane for the separation of substance mixtures described in DE 19836418 A1: Both allow for a high substance throughput, but, however, are permeable only for molecules with molecule masses up to a maximum of
25  approx. 1000 g/mol.
The permeation behavior of small molecules through polymer films has been very thoroughly examined, namely for gasses as well as liquids(J. Crank, G.S. Park, "Diffusion in Polymers", Academic Press, N.Y., 1968; J. Comyn Ed., Polymer
30  Permeability, Elsevier Appl. Sci. London , 1986; H.B. Hopfenberg, V. Stannett in "The Physics of Glassy Polymers", R.N. Haeward Ed. Applied Science Publ. London, 1973, p. 504; T.V. Naylor in "Comprehensive Polymer Science", S.G.Allen Ed., Pergamon Press, N.Y., 1989; F. Bueche, "Physical

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Properties of Polymers", Interscience Publ. N.Y. (1962);
H.G.Elias, "Makromoleküle", Hüthig und Wepf, Basel (1975)).

None of the aforementioned methods, however, allows for the
5  separation of macromolecules with high selectivity and high
throughput quantity.

Surprisingly, and in contradiction with the technical state
of the art hitherto, it was established that long chain
10  molecules can diffuse not only through polymer films, so that
a separation of macromolecules by polymer films is possible.
The separation effect of the polymer film, therefore, depends
on the permeation of the substances to be separated and,
hence, the reptation in combination with the solubility of
15  the permeants in the polymer film.

The object of the current invention is to provide a method
that allows for the separation of macromolecules from their
mixtures of low and high molecular substances with high
20  selectivity and/or high throughput quantity for the first
time.
According to the present invention, this object is achieved
by a method according to Claim 1 using at least one non-
porous polymer film, whereby the temperature of this at least
25  one non-porous polymer film is equal to or greater than the
glass transition temperature $T_G$ of this at least one non-
porous polymer film, and whereby under non-porous, those
films are meant which have pores that do not completely
impenetrate from one side to the other. The polymer films
30  defined as "non-porous" according to the above definition can
also be considered as closed polymer films.

A further object of the invention is to provide a suitable
separation medium for the separation of macromolecules from

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their mixture of low-/high-molecular substances, whereby this separation medium allows for the separation of macromolecules from their mixture of low-/high-molecular substances with high selectivity and/or high throughput quantity. According

5  to the present invention, this object is achieved through use of separation media containing at least one non-porous polymer film according to Claim 26, whereby under non-porous, those films are meant which have pores that do not completely impenetrate from one side to the other.

10

Surprisingly, and in contradiction to currently existing publications, it was found that it is possible to separate polymer systems, effectively and in large quantities, by means of the permeation of polymer systems through a non-

15  porous polymer film.
These polymer films allow macromolecules to permeate from one side of the film, around the chain molecules in the film, to the other side of the film. During this permeation process, macromolecules diffuse around the long chain molecules of

20  which the polymers consist. This permeation process is also referred to as reptation, wherein one understands reptation as being the curvilinear movement along a chain, around the hindrances. During this, a separation process with respect to molecular weight, chain architecture and particle shape

25  arises. Hence, the non-porous polymer films are suitable for separating macromolecules from their mixtures with low and high molecular substances.
The requirement for permeation or reptation is an adequate mobility of the molecules of which the polymer film consists

30  or which the polymer film contains. It is known to the person skilled in the art that all polymers – also those that are crystalline as well as semi-crystalline – contain amorphous regions.

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In combination with the present invention, within the framework of the research which led to the current invention, it was found that the amorphous regions of non-porous polymer films are sufficiently mobile after reaching the glass

5 transition temperature $T_G$ to allow macromolecules to permeate through this film.

Within the framework which led to the current invention, it was found that no swelling of the polymer film with a liquid medium is necessary before permeation if the glass transition

10 temperature $T_G$ of the non-porous polymer film employed as the separating agent is under the temperature at which the separation of macromolecules is conducted (separation temperature). Furthermore, it was found during the research connected to the current invention that glass transition

15 temperatures $T_G$ of amorphous regions above the separation temperature can be lowered to $T_G$-values beneath the separation temperature through swelling with a liquid medium in order to allow for the permeation of macromolecules through the polymer film.

20

The method according to the present invention, for the separation of macromolecules from their mixtures with low and high molecular substances, separates these systems through film permeation (FP) in regard to molecular weight and/or

25 chemical structure of the chain molecules and/or chemical structure of the chain molecules in mixtures and/or the degree of branching and/or the chain architecture, and/or it is suitable for the separation of flexible ball-shaped macromolecules from stiff-chain rod-shaped macromolecules

30 and/or for the separation of linear and cyclic macromolecules and/or for the separation of chemical impurities in synthetic materials (monomers, oligomers, byproducts of the synthesis) and/or for the separation of catalysts, colloidal additives

and other additives, wherein a high throughput quantity of
the mixture to be separated is achieved in short timeframes.

Great amounts of macromolecules can be separated from their
5    mixtures with low- and high-molecular substances.
The polymer films that can be utilized in the separation
method according to the present invention are produced via
methods known to the person skilled in the art by means of
chemical vapor deposition (CVD), plasma polymerization, spin-
10   coating, sublimation, doctor blading, spraying, or extrusion.

The films utilized as separation media are crystalline, semi-
crystalline, or amorphous, chemically cross-linked or non-
cross-linked; they can be copolymers, block copolymers, or
15   polymer alloys; they can consist of several films or several
polymers of different chemical structures that exist as
multi-layer films or tandem systems, feature a chemical
gradient in which the chemical composition changes
systematically throughout the film, consist of reactive
20   polymers that are capable of chemical reactions such as
cross-linking and/or binding specific groups, feature a
special surface topology (rough and/or porous surface,
wherein the pores do not permeate the film completely from
side to side), contain solid flux (carbon black, mica, chalk,
25   etc.), be coated on or between porous substrates (inorganic
or organic porous membranes or tissue), and/or exist in the
form of hollow fibers. Where films consisting of hollow
fibers are utilized as separation media, the permeation of
the mixture to be separated takes place through the walls of
30   the hollow fibers. Multi-layer films as separation medium are
films that consist of at least two layers of identical or
different polymers, with no space between two layers in each
case. Tandem configurations are systems in which several
permeation configurations are arranged one after the other or

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parallel with liquid media between the polymer films utilized
as separation media and arranged one after the other and/or
parallel.

5   Suitable polymer films consist of and / or contain polymers
such as poly-(p-xylylene), polyvinylidene halides, polyester,
polyether, polyolefins, polycarbonates, polyurethanes,
natural polymers, polycarboxylic acids, polysulfonic acids,
sulphated polysaccharides, polylactides, polyglycosides,
10  polyamides, polyvinylalcohols, poly-α-methylstyrenes,
polymethacrylates, polyacrylnitriles, poly-(p-xylyles),
polyacrylamides, polyimides, polyphenylenes, polysilanes,
polysiloxanes, polybenzimidazoles, polybenzthiazolenes,
polyoxazoles, polysulfinides, polyesteramides,
15  polyarylenvinylenes, polyetherketones, polyurethanes,
polysulfones, ormocerenes, polyacrylates, silicones, fully
aromatic copolyesters, poly-N-vinylpyrrolidones,
polyhydroxyethylmethacrylates, polymethylmethacrylates,
polyethylenterephthalates, polymethacrylnitriles,
20  polyvinylacetates, neoprene, Buna N, polybutadienes,
polytetrafluorethylenes, modified or unmodified celluloses,
α-olefins, vinylsulfonic acids, maleic acids, alginates or
collagens.

25  The monomers that form the basis of the polymers can each
support one or more functional groups, while, in each case,
they can be of one or different types of substituents. This
relates to the following functional groups:
H, linear or branched alkyl, alkenyl, alkinyl, cycloalkyl,
30  cycloalkenyl, cycloalkinyl, phenyl, phenylalkyl,
phenylalkenyl, phenylalkinyl, phenylcycloalkyl,
phenylcycloalkenyl, phenylcycloalkinyl, cycloalkyl-alkyl,
cycloalkyl-alkenyl, cycloalkyl-alkinyl, heterocyclic
compounds, heterocyclo-alkyl, heterocyclo-alkenyl,

heterocyclo-alkinyl, linear or branched alkylsulphonate,
alkenylsulphonate, alkinylsulphonate, linear or branched
alkylbenzenesulphonate, alkenylbenzenesulphonate,
alkinylbenzenesulphonate, aminosulphonyl-alkyl,

5  aminosulphonyl-alkenyl, aminosulphonyl-alkinyl,
aminosulphonyl-cycloalkyl, aminosulphonyl-cycloalkenyl,
aminosulphonyl-cycloalkinyl, linear or branched alkyl-
sulphonamide, alkenyl-sulphonamide, alkinyl-sulphonamide,
cycloalkyl-sulphonamide, cycloalkenyl-sulphonamide,

10  cycloalkinyl-sulphonamide, phenyl-sulphonamide, heterocyclo-
sulphonic acid, heterocyclo-sulphonamide, heterocyclo-alkyl-
sulphonic acid, heterocyclo-alkyl-sulphonamide, heterocyclo-
alkenyl-sulphonic acid, amide- or ester-like bound linear
and/or branched-chain aliphatic sulphonic, carboxylic and/or

15  phosphonic acid, styrene sulphonic acid, anetol sulphonic
acid, styrene phosphonic acid, heterocyclo-alkenyl-
sulphonamide, heterocyclo-alkinyl-sulphonic acid,
heterocyclo-alkinyl-sulphonamide, aryl-sulphonic acid, aryl-
sulphonamide, aryl-alkyl-sulphonic acid, aryl-alkyl-

20  sulphonamide, aryl-alkenyl-sulphonic acid, aryl-alkenyl-
sulphonamide, aryl-alkinyl-sulphonic acid, aryl-alkinyl-
sulphonamide, alkyl-, alkenyl, alkinyl-, aryl-, heteroalkyl-,
heteroaryl-carboxylic acids, esters thereof, carboxylic acid
amides thereof, amino acids, orthologous phosphonic acid

25  derivatives of all sulphonic acids listed, hydroxy-alkyl-,
hydroxy-alkenyl-, hydroxy-alkinyl-, hydroxy-cycloalkyl-,
hydroxy-alkyl-cycloalkyl-, hydroxy-cycloalkyl-alkyl-,
hydroxy-phenyl-, hydroxy-alkyl-phenyl-, hydroxy-phenyl-alkyl-
groups as well as the orthologous amino- and thio- compounds,

30  polyethoxy-alkyl, polyethoxy-alkenyl, polyethoxy-alkinyl,
polyethoxy-cycloalkyl, polyethoxy-cycloalkenyl, polyethoxy-
cycloalkinyl, polyethoxy-aryl, polyethoxy-alkyl-aryl,
polyethoxy-heterocycloalkyl, polyethoxy-heterocycloaryl,
alkanal, alkenal, alkinal, cycloalkenal, benzene

carbaldehyde, heteroaryl-carbaldehyde, benzyl-alkyl-carbaldehyde, heteroaryl-carbaldehyde, aliphatic heteroalkyl-alkenal, hetero-alkenyl-alkenal, hetero-alkinyl-alkenal, alkanon, alkenon, alkinon, cycloalkyl-alkanon,

5  dicycloalkanon, arylalkanon, heteroaryl-alkanon, imines, halogens and halogenated derivatives of all groups listed, nitriles, isonitriles, sulphonic acid esters, phosphonic acid esters, nitro compounds, hydroxylamines, allyl compounds, adenosine-3',5'-monophosphate, adenosine-3',5'-diphosphate,

10  adenosine-3',5'-triphosphate, guanosine-3',5'-monophosphate, guanosine-3',5'-diphophate, guanosine-3',5'-triphosphate, dextran sulphate cellulose, cation exchanging groups, anion exchanging groups. Preferably, therein,

- alkyl stands for a group with 1-20 carbon atoms

15  - alkenyl und alkinyl stand for a mono- or polyunsaturated group with 3-20 carbon atoms

- the heterocyclic groups stand for an R group with 1-20 carbon atoms, wherein up to 5 carbon atoms can be replaced by hetero atoms which are selected from the

20  group nitrogen, oxygen, sulfur, phosphorus

- aryl stands for an aromatic R group with 5-20 carbon atoms

- heteroaryl stands for a corresponding aromatic R group in which up to 5 carbon atoms can be replaced

25  by hetero atoms from the group nitrogen, oxygen, sulfur, phosphorus.

Subsequently, the polymer films – e.g. equipped with gaskets if necessary – are typically built into a two-chamber or

30  multiple-chamber configuration. The chambers are filled with a solvent on the one side (analysis chamber), and with a solution of the same or some other solvent containing the permeants on the other side (sample chamber) or, when the permeants are liquid, they can be brought into the sample

chamber without an additional solvent. In the case of the
utilization of tandem systems, several permeation
configurations are aligned parallel and/or one after the
other, wherein, between the polymer films that are utilized
5  as separation media and aligned one after the other and/or
parallel, there are liquid media in the form of solvents or
mixtures of solvents.
The solvent or mixture of solvents can consist of protic,
aprotic, aqueous, aliphatic, aromatic, heteroaliphatic,
10 heteroaromatic, alicyclic and/or heteroalicyclic liquids.

Subsequently, the permeation of the permeation mixture's
components takes place, wherein permeation velocity depends
on the physicochemical properties of each component and
15 thereby allows for a separation of the mixture. In the
analysis chamber, which is initially free from polymer
components, the pure singular components of the mixture can
be extracted selectively according to their chronological
arrival.
20

The separation method can be carried out continuously or
discontinuously by means of the method known to a person
skilled in the art in combination with light dispersion,
25 viscosimetry, UV-Vis spectroscopy, gel permeation
chromatography (GPC) or solvent precipitation or at a
pressure adjusted in a controlled manner.

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**Practical embodiment 1: Films suitable for polymerpermeation**

Reference example 1: Poly-(p-xylylene) films (PPX)
PPX films were produced via the CVD technique (chemical vapor
5  deposition) known to the person skilled in the art in the
thicknesses desired ranging from 500 nm to 5 µm. This
technique ensures the production of non-porous films.

Reference example 2: Polyvinylidene fluoride films (PVDF)
10  PVDF films were produced from solution at increased
temperatures (ranging from 40 to 80°C) via the spin-coating
technique known to the person skilled in the art. Films with
thicknesses of between 500 nm and 3.6 µm were produced.

15  Reference example 3: Polyethylene films (PE)
Technical PE films with thicknesses in the range of 100 µm
were employed.

20  **Practical embodiment 2: Permeation configuration**

Reference example 4: Configuration for experiments on a
laboratory scale

25  The films – equipped with gaskets – were inserted into a two-
chamber configuration, wherein the surface area of the films
was in the range of few cm$^2$ (cf. Fig 1).The chambers were
filled with a solvent on the analysis side and with a
solution containing the respective mixture of permeants on
30  the sample side. The volume of the sample amounted to approx.
40 ml, and the polymer concentration was in a range of 1-10%.

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**Practical embodiment 3: Permeations**

Reference example 5: Permeation of chloroform through a PPX
film

5    A PPX film with a thickness of 3.6 µm and a diameter of 2 cm
was utilized. Approx. 40 ml of deuterated chloroform was
filled into the analysis chamber of the permeation apparatus;
the sample chamber was filled with the same volume of non-
deuterated chloroform. As a standard reference, a defined

10   amount of methanol was utilized. The permeation of non-
deuterated chloroform into the analysis chamber was
determined by means of a $^1$H-NMR measurement. What was
recognizable was an initial phase caused by a swelling of the
PPX film, followed by a permeation phase (cf. Fig. 2).

15


Reference example 6: Permeation of acetone through a PPX film
A PPX film with a thickness of 3.6 µm and a diameter of 2 cm
was utilized. Approx. 40 ml of deuterated acetone was filled

20   into the analysis chamber of the permeation apparatus; the
sample chamber was filled with the same volume of non-
deuterated acetone. As a standard reference, a defined amount
of methanol was utilized. The permeation of non-deuterated
acetone into the analysis chamber was determined by means of

25   a $^1$H-NMR measurement. Within a 36-hour time period after the
beginning of the test series, no increase in the
concentration of acetone could be found in the chamber with
deuterated acetone. Permeation did not occur, the test series
was cancelled. The result is consistent to theory since

30   acetone should not swell PPX.


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Reference example 7: Permeation of polyethylene oxide through
a PPX film

A PPX film with a thickness of 3.6 µm and a diameter of 2 cm
was utilized. The sample chamber was filled with a solution

5   of polyethylene oxide (hydroxy end groups, molecular weight
200g/mol = PEO 200) in deuterated chloroform, the analysis
chamber was filled with the same solvent volume of pure
deuterated chloroform. By taking samples from the analysis
chamber and a subsequent ^{1}H-NMR spectroscopy, the permeation

10  of PEO 200 was determined. It was clearly discernible that
PEO 200 cannot be detected inside the analysis chamber until
after approx. 160 hours. After approx. 400 hours, approx. 0.5
g of PEO 200 had permeated through the PPX membrane (cf. Fig.
3).

15

Reference example 8: Permeation of polyethylene oxide through
a PPX film

A PPX film with a thickness of 2.4 µm and a diameter of 2 cm
was utilized. The sample chamber was filled with a solution

20  of polyethylene oxide (hydroxy end groups, molecular weight
200g/mol = PEO 200) in deuterated chloroform; the analysis
chamber was filled with the same solvent volume of pure
deuterated chloroform. By taking samples from the analysis
chamber and subsequent ^{1}H-NMR spectroscopy, the permeation of

25  PEO 200 was determined. It was clearly discernible that PEO
200 can already be detected inside the analysis chamber after
a few minutes. After approx. 400 hours, approx. 2.5 g of PEO
200 had permeated through the PPX membrane (cf. Fig. 4).

30  Reference example 9: Permeation of polyethylene oxide through
a PPX film

A PPX film with a thickness of 1.3 µm and a diameter of 2 cm
was utilized. The sample chamber was filled with a solution
of polyethylene oxide (hydroxy end groups, molecular weight

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200g/mol = PEO 200) in deuterated chloroform, the analysis chamber was filled with the same solvent volume of pure deuterated chloroform. By taking samples from the analysis chamber and a subsequent ^{1}H-NMR spectroscopy, the permeation
5 of PEO 200 was determined. It was clearly discernible that PEO 200 can already be detected inside the analysis chamber after a few minutes. After approx. 400 hours, approx. 2.9 g of PEO 200 had permeated through the PPX membrane (cf. Fig. 5).
10

Reference example 10: Permeation of a polystyrene mixture through a PPX film

A PPX film with a thickness of 1.3 µm and a diameter of 2 cm was utilized. The sample chamber was filled with a mixture of
15 polystyrene (molecular weight 3,600g/mol = PS36) and polystyrene (molecular weight 1,500,000 g/mol = PS 1.5), dissolved in chloroform.

The extracted samples were examined by means of a gel permeation chromatography (GPC). Gel permeation
20 chromatographies of the initial mixture (cf. Fig. 6) and of the permeate extracted after 24 hours (cf. Fig. 7) showed that the polymers could distinctly be separated by means of the GPC. The sample taken after 24 hours distinctly showed that only PS36 had permeated through the PPX membrane,
25 whereas the more highly molecular PS 1.5 had not reached the analysis chamber.


Reference example 11: Permeation of decane through an LDPE
30 film

A film made of low density polyethylene (LDPE), with a thickness of 100 µm and a diameter of 2 cm, was utilized. 85g of $CDCl_3$ and 2.99g of decane ($C_{10}$) were brought into the sample chamber. The analysis chamber was filled with 80g of

pure CDCl$_3$. After approx. 350 hours, approx. 1.0g of decane had permeated (cf. Fig. 8). The decane that had permeated into the analysis chamber was verified by means of a $^1$H-NMR spectroscopy.

5

Reference example 12: Permeation of squalane through an LDPE film

A film made of LDPE, with a thickness of 100 μm and a

10 diameter of 2 cm, was utilized. 2.97 g of squalane (C$_{30}$) were dissolved in 80g of chloroform and inserted into the sample chamber. The squalane which had permeated into the analysis chamber was verified by means of a $^1$H-NMR spectroscopy. Within approx. 350 hours, approx. 0.04 g of squalane

15 permeated through the LDPE membrane (cf. Fig. 9).

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**Reference numeral list**

Figure 1:

5 1. Sample chamber with the dissolved mixture of permeants

2. Polymer film and/or polymer membrane

3. Analysis chamber with a (pure) solvent and/or a (pure) mixture of solvents

4. Permeation of the permeant/s through the polymer film

10  and/or the polymer membrane

5. Permeation of the solvent/ mixture of solvents through the polymer film and/or the polymer membrane

15 Figure 2: Permeation of chloroform through a PPX film

Permeation of chloroform through a PPX film with a thickness of 3.6 µm at a diameter of 2 cm. In the sample chamber, approx. 40 ml of non-deuterated chloroform were provided, in the analysis chamber, approx. 40 ml of deuterated chloroform

20 were Provided. The concentration distribution of the non-deuterated chloroform's permeation was determined by means of a $^1$H-NMR measurement. A. defined amount of methanol served as a standard reference.

X axis: time measured in minutes

25 Y axis: portion of the non-deuterated chloroform in the
   analysis chamber containing only
   deuterated chloroform initially (V/V)

Figure 3: Permeation of PEO 200 through a PPX film with a

30 thickness of 3.6 µm

Permeation of PEO 200 through a PPX film with a thickness of 3.6 µm and a diameter of 2 cm. The sample chamber was filled with a solution of approx. 40 ml of polyethylene oxide in deuterated chloroform; the analysis chamber was filled with

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approx. 40 ml of deuterated chloroform. The permeation of PEO 200 into the analysis chamber was determined by means of a ^{1}H-NMR measurement.

X axis: time measured in hours

5 Y axis: amount of the PEO 200 permeated through the PPX membrane in g


Figure 4: Permeation of PEO 200 through a PPX-Film with a thickness of 2.4 μm

10 Permeation of PEO 200 through a PPX film with a thickness of 2.4 μm and a diameter of 2 cm. The sample chamber was filled with a solution of approx. 40 ml of polyethylene oxide in deuterated chloroform, the analysis chamber was filled with approx. 40 ml of deuterated chloroform. The permeation of PEO 15 200 into the analysis chamber was determined by means of a ^{1}H-NMR measurement.

X axis: time measured in hours

Y axis: amount of PEO 200 permeated through the PPX membrane


20 Figure 5: Permeation of PEO 200 through a PPX film with a thickness of 1.3 μm

Permeation of PEO 200 through a PPX film with a thickness of 1.3 μm and a diameter of 2 cm. The sample chamber was filled with a solution of approx. 40 ml of polyethylene oxide in 25 deuterated chloroform, the analysis chamber was filled with approx. 40 ml of deuterated chloroform. The permeation of PEO 200 into the analysis chamber was determined by means of a ^{1}H-NMR measurement.

X axis: time in hours

30 Y axis: amount of PEO 200 permeated through the PPX membrane in g


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Figure 6: Gel permeation chromatography of a mixture of PS 36
und PS 1.5 in chloroform
Gel permeation chromatogram of a mixture of PS 36 and PS 1.5
(initial concentration: 0.05 g/l, maximal elution time = 110
5   minutes). The figure shows the separation of the two
components of the polymer mixture.
X axis: elution time (min)
Y axis: detector signal (mV)


10  Figure 7: Selective Permeation of PS 36 through a PPX film,
determined by means of GPC measurements
Permeation of a mixture of PS 36 and PS 1.5 through a PPX
film with a thickness of 1.3 µm and a diameter of 2 cm. The
sample chamber was filled with approx. 40 ml of a mixture of
15  the two polymers in deuterated chloroform; the analysis
chamber was filled with approx. 40 ml of deuterated
chloroform. The samples extracted from the analysis chamber
were examined by means of a GPC after 24 hours. At this
point in time, PS 36 was found exclusively in the permeate.
20  X axis: elution time
Y axis: detector signal (mV)


Figure 8: Permeation of decane through an LDPE film
25  Permeation of decane through an LDPE film with a thickness of
100 µm and a diameter of 2 cm. 85 g of chloroform and 2.99 g
of decane were inserted into the sample chamber. The analysis
chamber was filled with 80 g of pure chloroform. The decane
that had permeated into the analysis chamber was determined
30  by means of a $^1$H-NMR measurement.
X axis: time in hours
Y axis: amount of the decane permeated altogether in g


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Figure 9: Permeation of squalane through an LDPE film

Permeation of squalane through an LDPE film with a thickness
of 100 µm and a diameter of 2 cm. 2.97 g of squalane in 80 g
5    of chloroform was inserted into the sample chamber. The
analysis chamber was filled with 80 g of pure chloroform. The
squalane that had permeated into the analysis chamber was
determined by means of a ^{1}H-NMR measurement.

X axis: time in hours

10   Y axis: amount of the squalane permeated altogether in g

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